

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

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PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference 234344	Date of Mailing (day/month/year) 14 MAR 2000
International application No. PCT/US99/07970	International filing date (day/month/year) 12 APRIL 1999
Applicant TRUSTEES OF PRINCETON UNIVERSITY	

1. ☒ The applicant is hereby notified that the international search report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIFO
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For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

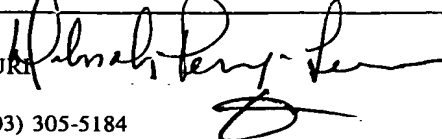
☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 bis 1 and 90 bis 3, respectively, before the completion of the technical preparations for international publication.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 234344	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US99/07970	International filing date (<i>day/month/year</i>) 12 APRIL 1999	(Earliest) Priority Date (<i>day/month/year</i>) 13 APRIL 1998
Applicant TRUSTEES OF PRINCETON UNIVERSITY		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 5 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (See Box I).
2. ☐ Unity of invention is lacking (See Box II).
3. ☐ The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing
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 - ☐ transcribed by this Authority.
4. With regard to the title,
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 - ☐ the text has been established by this Authority to read as follows:
5. With regard to the abstract,
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 - ☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. The figure of the drawings to be published with the abstract is:
Figure No. 12 b
 - ☐ as suggested by the applicant.
 - ☐ because the applicant failed to suggest a figure.
 - ☒ because this figure better characterizes the invention.
 - ☐ None of the figures.

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US99/07970**Box III TEXT OF THE ABSTRACT** (Continuation of item 5 of the first sheet)

The methods of this invention involve modification of an organic film after it has been deposited by either adding new dopants into it from top or bottom surface, or by causing dopants to leave the film from its top or bottom surface. In the examples of these methods, the emitting color of light emitting diodes are modified based on doped polymers by locally introducing dopants causing different color emission into the film by local application of a solution containing desired dopant to the film surface (by ink-jet printing, screen printing, local droplet application, etc.). This covers the difficulties of encountered with direct patterning of three separately formed organic layers (each which uniformly coats an entire surface when formed) into regions for separate R, G, and B devices due to sensitivities of the organic materials to chemicals typically used with conventional patterning technologies. Alternatively, dopants may be introduced in an organic film (16) by diffusion from one layer (18, 19) into the film(16). Alternatively, dopants may be selectively removed from a film with solvents, etc.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/07970

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : HOIL 33/00, HOIL 21/48, HOLI 2/76; HOIL 21/223, HOLI 21/225

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 438/ 22,23, 35,45, 99, 542,548, 562, 956
257/79, 89,103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
INSPEC, CA, WEST/BRIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,681,756 A (NORMAN et al) 28 OCTOBER 1997 (28.10.97)(see abstract, fig.6	1-36
X	US 5,116,781 A(AGOSTINELLI et al) 26 MAY 1992(26.05.92)see abstract, col. 3, lines 38-65, col. 4, lines 44-68, col 5, lines 5-17.	9,10 1-8, 15-36
A	US 4,104,091 A (EVANS et al) 01 AUGUST 1978 (01.08.78)see abstract	1-36
X A	US 4,251,285 A(YOLDAS ET AL) 17 FEBRUARY 1981(17.02.81)See abstract detailed description	9 1-8, 10-36
X A	US 3,615,943 A (GENSER) 26 OCTOBER 1971 (26.10.71)see abstract	9 1-8,10-36

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

11 FEBRUARY 2000

Date of mailing of the international search report

14 MAR 2000

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SAVITRI MULPURI

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/07970

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US 5,972,052 A(KOBAYASHI et al) 26 OCTOBER 1999(26.10.99)see abstract, fig. 4.	1-36
A, P	US5,866,922 A(HUANG et al) 02 FEBRUARY 1999 (02.02.99)see abstract, fig.8	1-36
A, P	US 5,953,587 A(FORREST et al) (14 SEPTEMBER 1999 (14.09.99)see abstract, fig. 2n	1-36
A	US 5,693,962 A(Shi et al) 02 DECEMBER 1997 (02.12.97)see abstract, summary of the invention	1-36
A	US 5,583,349 A(NORMAN et al) 10 DECEMBER 1996 (10.12.96)see abstract	1--36

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/07970

A. CLASSIFICATION OF SUBJECT MATTER:
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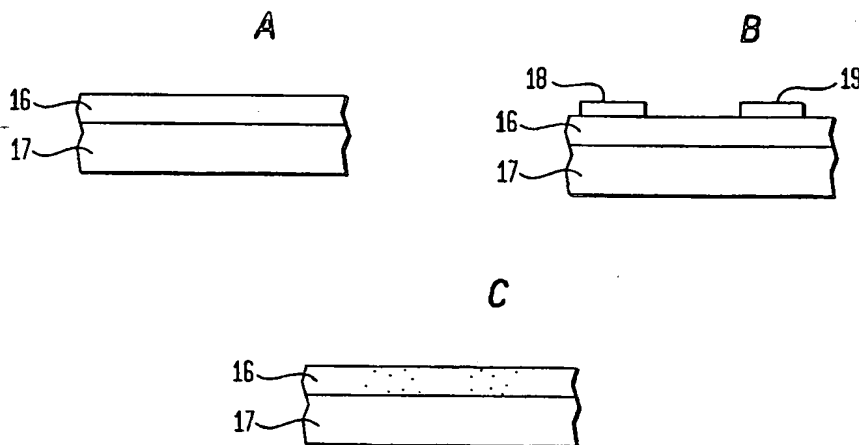
438/ 22,23, 35,45, 99, 542,548, 562, 956
257/79, 89,103



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US99/07970 (22) International Filing Date: 12 April 1999 (12.04.99) (30) Priority Data: 60/081,492 13 April 1998 (13.04.98) US (71) Applicant (for all designated States except US): TRUSTEES OF PRINCETON UNIVERSITY [US/US]; P.O. Box 36, Princeton, NJ 08544-0036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): STURM, James, C. [US/US]; 3R Magie Apartment, Faculty Road, Princeton, NJ 08540 (US). HEBNER, Thomas, R. [US/US]; 214G Halsey Street, Princeton, NJ 08540 (US). (74) Agent: FRISCIA, Michael, R.; Friscia & Nussbaum, One University Plaza, Hackensack, NJ 07601 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>

(54) Title: MODIFICATION OF POLYMER OPTOELECTRONIC PROPERTIES AFTER FILM FORMATION IMPURITY ADDITION OR REMOVAL

**(57) Abstract**

The methods of this invention involve modification of the properties of an organic film after it has been deposited by either adding new components into it from its top or bottom surface, or by causing components to leave the film from its top or bottom surface. In the examples of these methods, the emitting color of light-emitting diodes are modified based on doped polymers by locally introducing dopants causing different color emission into the film by local application of a solution containing the desired dopant to the film surface (by ink jet printing, screen printing, local droplet application, etc.). This overcomes difficulties encountered with the direct patterning of three separately formed organic layers (each which uniformly coats an entire surface when formed) into regions for separate R, G, and B devices due to the sensitivities of the organic materials to chemicals typically used with conventional patterning technologies. Alternatively, dopants may be introduced in an organic film by diffusion from one layer into the film. Alternatively, dopants may be selectively removed from a film with solvents, etc.

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MODIFICATION OF POLYMER OPTOELECTRONIC PROPERTIES
AFTER FILM FORMATION IMPURITY ADDITION OR REMOVAL

5

SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to methods of making semiconductor devices using light emitting organic materials, and more specifically, to methods which involve the modification of the properties of an organic film after it has been deposited by either: (i) adding new components into the film from a top or bottom surface; or (ii) by causing components to leave the film from a top or bottom surface.

15

RELATED ART

Polymers and blends of polymers and small organic molecules have recently been extensively used to fabricate organic light emitting diodes and thin film transistors.

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Organic films are typically deposited in thin film form for electrical and optoelectronic applications by uniformly coating a surface by spin-coating or other methods. Sometimes the final organic film itself is not directly formed, but a precursor is deposited which is converted to a polymer by a subsequent step, such as heating or exposure to UV light (e.g. PPV). It is also well known that adding various elements to the organic film can change its electrical and/or optical properties. These may include elements to change the conduction of electrical carriers (e.g. PBD for electron transportability), or dye centers to change the color of photo- and electro-luminescence (e.g. coumarin 6 in PVK). These extra elements are usually added to the original material before the final solid film is deposited. For example, these different groups could be bonded to a polymer chain before the polymer is deposited by spin coating, or may just be added as other polymers or individual smaller molecules to the solution containing the polymer before a thin film is formed. In either case all materials in the original solution become part of the final film.

35

The goal of fabricating full color flat panel displays has the potential to be reached using organic light emitting diodes (OLEDs). The difficulty with using this technology is that the current deposition techniques, such as spin-coating and evaporation, deposit blanket films. The film can be used to make devices of a single color. To achieve individual emitters of different color next to each other, such as red, green, and blue, the deposited blanket film must be typically etched into a pattern, as might be done by photolithography followed by etching. Then, this process has to be repeated for multiple layers to achieve full color (red, green and blue emitters). Etching of organic films and photoresist processing for lithography on organic films has proven to be technically very difficult and expensive. Therefore, instead of making a blanket film of one color, etching and making a blanket film of another color, it would be beneficial to make one blanket film and later locally change the properties of the film to emit different light colors. Thus, the need for etching would be removed.

Another approach is ink-jet printing local regions, but a problem associated with ink-jetting printing is that the dots printed do not have a uniform thickness.

Accordingly, what is desired, and has not heretofore been developed, is a method to modify the properties of a film after it has been formed, by introducing therein or removing impurities to modify the properties therefrom.

OBJECTS AND SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for manufacturing optoelectronic organic films having locally modified areas.

5 Another object of the present invention is to provide an organic film with various regions of modified optoelectronic properties.

Still another object and advantage of the invention is to form an organic film with modified properties by applying dopants in desired places.

10 A further object and advantage of the invention is the provision of a method for forming an organic film with local modified areas by adding impurities to or removing impurities from the film.

Even another object of the invention is to provide a method for locally modifying properties of an organic film without the need for photolithography and etching of the organic film.

15 A still further object and advantage of the invention is the provision of a method for manufacturing a locally modified organic film with the need for contacting the surface of said film with solvents.

20 Even an additional object of the invention is to provide a process of forming a locally modified organic film wherein dopant is added to the film in an annealing process.

Yet an additional object of the present invention is to provide a process for transferring a dopant from one layer to another layer.

A further object of this invention is the provision of a process for transferring a dopant from one layer to another layer in a desired pattern.

25 The methods of this invention involve modification of the properties of an organic film after it has been deposited by either adding new components into it from its top or bottom surface, or by causing components to leave the film from its top or bottom surface. In the examples of these methods, the emitting color of light-emitting diodes are modified based on doped polymers by locally
30 introducing dopants causing different color emission into the film by local application of a solution containing the desired dopant to the film surface (by ink jet printing, screen printing, local droplet application, etc.). This overcomes difficulties encountered with the direct patterning of three separately formed

organic layers (each which uniformly coats an entire surface when formed) into regions for separate R, G, and B devices due to the sensitivities of the organic materials to chemicals typically used with conventional patterning technologies. Alternatively, dopants may be introduced in an organic film by diffusion from one
5 layer into the film in local regions or by locally applying them directly into the organic film. Alternatively, dopants may be selectively removed from a film with solvents, etc.

Typically all of the active components are incorporated into the polymer when the polymer film is first formed, for example by spin coating it over a
10 surface. In the present invention, the properties of the material are modified after a solid film has been formed by later introducing new species into the film from either its top or bottom surface, or removing impurities out through the top or bottom surface especially in a patterned arrangement. The method is especially attractive for the local modification of the photoluminescence and/or
15 electroluminescence color of a thin film of the material, for example to create red, green, and blue light-emitting regions after a surface has been coated with a thin film of the material which is the same everywhere.

BRIEF DESCRIPTION OF THE DRAWINGS

Other important objects and features of the invention will be apparent from the following Detailed Description of the Invention taken in connection with the accompanying drawings in which:

FIGS. 1a and 1b are diagrams of the application of dye on top of PVK film.

FIGS. 2a and 2b are diagrams of dye on PVK film under UV illumination.

FIG. 3 is a plot of photoluminescence of materials used in **FIGS. 1-2**.

FIG. 4a is a diagram of a device and **FIG. 4b** is a plot of the electroluminescence spectra of PVK and C6.

FIGS. 5a and 5b are diagrams of removal of local dye with acetone.

FIG. 6a is a diagram of a device and **FIGS. 6b and 6c** photographs of the device of **FIG. 6a** under UV illumination.

FIG. 7 is a photograph under UV illumination of a device fabricated with an ink jet printer;

FIG. 8a is an experiment showing the effects of temperature on devices fabricated in accordance with the invention, and **FIG. 8b** is plot thereof.

FIG. 9 is a photograph under UV illumination of a device formed in accordance with the invention at increasing temperatures.

FIGS. 10a - 10c illustrate the steps in introducing film dopants from the top.

FIGS. 11a - 11c illustrate the steps in introducing dopants from the bottom.

FIGS. 12a -12c illustrates the steps for spatially modifying properties of polymer film.

FIGS. 13a - 13b illustrate the spectra of PVK and PVK with C6.

FIGS. 14a - 14c illustrate the steps in removing dopant from a polymer film into the underlying layer.

FIGS. 15a - 15c illustrate the steps in forming patterned addition of dopant from the top.

FIGS. 16a - 16c illustrate the steps in fabrication of patterned OLEDs.

FIGS. 17a - 17d illustrate the steps in fabrication of a passive matrix.

FIGS. 18a - 18c illustrate the steps in removal of dopant from polymer film in a pattern to the underlying layer.

5 **FIGS. 19a - 19b** illustrate the steps in removal of dopant from the top of a film.

FIGS. 20a - 20c illustrate the steps in the patterned removal of dopant from the top of a film.

10 **FIGS. 21a - 21d** illustrate the steps in fabrication of an active matrix OLED display.

DETAILED DESCRIPTION OF THE INVENTION

The goal of fabricating full color flat panel displays has the potential to be reached using organic light emitting diodes (OLEDs). The difficulty with using this technology is that the current deposition techniques, such as spin-coating and evaporation, deposit blanket films. The film can be used to make devices of a single color. To achieve individual emitters of different color next to each other, such as red, green, and blue, the deposited blanket film must be typically etched into a pattern, as might be done by photolithography followed by etching. Then, this process has to be repeated for multiple layers to achieve full color (red, green and blue emitters). Etching of organic films and photoresist processing for lithography on organic films has proven to be technically very difficult and expensive. Therefore, instead of making a blanket film of one color, etching and making a blanket film of another color, it would be beneficial to make one blanket film and later locally change the properties of the film to emit different light colors. Thus, the need for etching would be removed.

The present invention, in a broad, general sense, relates to the application of an organic film and thereafter modifying local characteristics thereof by adding or removing components, i.e. dopants, dyes, etc., to or from the film to change the local characteristics of the film. Specifically, the invention relates to modifying the optoelectronic properties of an organic film by impurity or additional removal in a patterned fashion after application of the film. Even more specifically, the invention relates to modifying the emitting color of light-emitting diodes based on doped polymers by locally introducing dopants causing different color emission into an organic film by local application of solutions containing desired dopants to the film surface, i.e. by ink-jetting or screen printing. Alternatively, impurities contained within the film prior to application can be removed therefrom in desired patterns through various methods such as by the application of solvents.

One way for achieving this result is to locally dye a poly(9-vinylcarbazole) (PVK a hole transporting polymer) spun-on film, with green, red and blue dyes. The dyes would dissolve in acetone or trichloroethylene (TCE), solvents that do not dissolve PVK, and could be patterned on top of the PVK film using an ink-jet printer. As shown in FIGS. 1a and 1b, the dopants diffuse into the film and the

solvent evaporates. Then metal cathodes could be patterned on top of the locally dyed regions, thus achieving full color integration.

To verify this technique, droplets of coumarin 6 (C6, a green dye) dissolved in TCE and Acetone were placed onto a spun-on 1000 angstrom thick PVK film using a pipette and the solvents were given time to evaporate. **FIG. 2a** shows a picture of these drops taken from above with a UV lamp shining on them to excite fluorescence of the organic film. Under UV, they appear to be a greenish yellow color. These droplets were also placed onto glass where no diffusion occurs and the C6 remains on the surface, and the solvents were allowed to evaporate, as shown in **FIG. 2b**. Under UV lamp they appear to be a reddish color. This indicates that when the drops are placed onto a PVK film there is some interaction with the PVK, because when the PVK is present the dyed areas appear greenish-yellow, and when the PVK is not present the dye appears red. The interaction is the diffusion of the dye into PVK.

In order to state the above observations in a more quantitative way, a photoluminescence spectra was taken. **FIG. 3** shows the PL spectra of a pure PVK film (peak at 410 nm), a PVK film locally dyed with C6 (peak at 490 nm), a blend film, where the PVK was dyed in solution with C6 (peak at 490 nm), and the dye on glass (peak at 580 nm). This provides evidence that not only does the dye interact with the PVK, but it interacts in such a way that the PL spectra is nearly identical to that of a blend film, which is known to be able to be made into a device. Therefore, the next step was to attempt to make a device using this locally dyeing procedure.

FIG. 4a shows the device structure, and **FIG. 4b** shows the electroluminescence (EL) spectrum of the device and the EL of a blend device made by dissolving PVK and C6 in chloroform, spinning the film, and evaporating contacts. To make the locally dyed device, PVK dissolved in chloroform was spun onto glass coated with indium tin oxide (ITO, a transparent conductor). Next, a drop of C6 dissolved in acetone was dropped onto the surface, the sample was then spun again. Finally, a metal contact was evaporated on top of the dyed area. The EL spectra of the locally dyed device is seen to have the same 490 nm peak as the blend device. Therefore, this shows that the dye not only interacts

with the PVK, but it interacts in such a way that a device can be made which has a similar EL spectra to blend device.

In order to further investigate this locally dyeing phenomenon, an experiment was set up to see if dye could be washed out of a blend film, which had been dyed in solution. **FIG. 5a** and **5b** shows a schematic of the experiment. First, PVK and C6 were dissolved in chloroform. Next, they were spun-on to an ITO coated glass substrate, forming a 1000 angstrom film. When this film was observed under a UV lamp, it appeared green. Next, a drop of acetone was dropped onto the surface. When a UV lamp was shone onto the sample, it was observed that where the drop of acetone had been, the sample was blue, and where it had not been, the sample was green. This indicates that the dye could be washed out of a blend film, which created a local area without dye. Therefore, two different color LEDs could be made on a substrate which had been locally washed.

FIG. 6a shows a schematic of the device made on the washed film. The film was prepared as mentioned above, and then metal cathodes were evaporated in the washed areas and in the non-washed areas. These cathodes were thermally evaporated and were patterned by a shadow mask. **FIGS. 6b** and **6c** are pictures of the devices, from below, emitting light. **FIG. 6b** shows a device emitting green (appears light blue because of camera used) and **FIG. 6c** shows an emitting blue. The green device is emitting green because the metal cathode was evaporated on top of the dyed film, and the blue device is emitting blue, because the metal cathode was evaporated on top of the washed film.

Thus, devices can be made by locally dyeing a PVK film, or by locally washing a dyed PVK film. Therefore, the next step is to pattern the dye using an ink-jet printer. **FIG. 7** shows a picture of a piece of glass coated with ITO, onto this glass was spun a 1000 angstrom thick film of PVK. Then an Epson Stylus Color 400 ink-jet printer was used to pattern C6 dissolved in acetone on top of the film. The sample was then illuminated under UV. This shows that the dyes can be patterned by an ink-jet printer with a spot diameter of ~500 μm . The next step is to try to determine the ultimate resolution of this technique.

An experiment was done to determine if the diameter of the printed spots could be influenced by temperature. **FIG. 8a** shows the experimental set-up, a 1000 angstrom film of PVK was spun onto a piece of glass coated with ITO. The sample was then placed onto a hot plate. Droplets of equal volume of C6 dissolved in acetone and equal volumes of C6 dissolved in TCE were dropped on to the PVK film at different temperatures. It was observed that at higher temperatures the spots did not spread as far and therefore had smaller diameters. This is shown in the plot of **FIG. 8b**. This could potentially make the spot size ~0.6 times smaller. However, this data does not reveal the difference observed in using TCE and acetone.

FIG. 9 shows a picture of the same spots dropped onto the PVK film at increasing temperatures lit up by a UV lamp. What can be seen is that there are, at higher temperatures in the TCE drops, bright yellow spots which are ~ 1/3 of the outer spot, and have a more intense luminescence. This may be because, as the solvent dries the C6 tends to stay in the solution and what is left at the end is a highly concentrated small diameter spot. When this spot profile is checked using a surface profilometer it is seen that the dye is actually sitting on the surface. Therefore, in order to take advantage of this small diameter, the substrate would have to be heated further, to allow the dye to thermally diffuse into the film.

In conclusion, PVK can be locally dyed by dissolving dye in acetone or TCE and dropping it on to the surface. Also, this dyed area can be made into a device. A blend film of PVK and C6 can have the C6 locally washed out of it using acetone, and a device can be made using this technique. At the present time ink-jet printed dyed lines can be made with widths of ~500 μm . This width can be further reduced by printing with TCE onto a heated substrate to obtain a spot 1/10 of the diameter of a spot made at room temperature. This substrate would have to then be heated again to thermally diffuse the dye into the film.

FIGS. 10a-10c illustrate the basic method for introducing film dopants from the top in the fabrication of red, green and blue OLED devices on a common substrate. As shown in **FIG. 10a**, a uniform film of polymer 10 without the desired dopant is formed on substrate 11. The polymer film 10 may contain other

dopants. In FIG. 10b, dopant 12 is placed on the surface of the polymer film 10 by evaporation, spin coating, or other method. In FIG. 10c annealing or other process caused the dopant 12 to enter the film 10 by diffusion or by other methods. The solvents used in spin coating the dopant 12 on the surface may cause dopant 12 to enter polymer 10 and be deposited into it without need for the steps described in FIG. 10c. In this case there is never a solid dopant layer on the surface.

FIGS. 11a-11c show the introduction of dopants into a film from the bottom thereof. In FIG. 11a, a substrate 13 has a coating 14 put down thereon. The coating 14 may contain the desired dopant or, the dopant may be applied in the manner described in FIGS. 10a-10c (i.e. may be polyaniline or similar hole transport layer in OLED). As shown in FIG. 11b, the polymer film 15 is deposited onto the coating 14. In FIG. 11c, annealing causes dopant to partially migrate from layer 14 into polymer film 15. It should be noted that the solvents used in spin coating the top polymer may "leach" dopant out of the underlying layer without the need for the thermal cycling described in FIG. 11c.

FIGS. 12a-12c show the steps of a method for spatially modifying the properties of the polymer film. FIG. 12a illustrates the deposition of a polymer 16 onto a substrate 17 in the same manner as discussed in connection with FIG. 10a. FIG. 12b shows the creation of local regions of different dopants, 18 and 19 on the polymer surface 16 by local deposition methods such as evaporation through different shadow masks, deposition by screen printing using different screens, or by ink jet printing, or other printing processes using different patterns for each dopant. FIG. 12c illustrates the heat treatment of the structures of FIG. 12b by annealing, for example, to cause the dopant 18 and 19 to migrate into the polymer 16. As discussed in connection with FIGS. 10a-10c, solvents used in screen printing or in ink jet printing may carry dopants directly into the polymer so that the heat treatment step of FIG. 12c may not be required.

This has been demonstrated using dyes C6 (green), C47 (blue), and Nile red (green) in acetone solution separately applied to individual regions of a single PVK film, where acetone solution is locally applied by an eyedropper or similar device. Acetone does not cause removal of PVK film, but after evaporation of

acetone in a few seconds the fluorescence color of the film under UV excitation has changed.

As illustrated in **FIGS. 13a-13b**, both the photoluminescence (**FIG. 13a**) and electroluminescence (**FIG. 13b**) show the shift between pure PVK film and
5 doped PVK.

The dopant need not be pure dopant, but may be co-deposited with another material. Subsequent process (or the very deposition process itself) can then cause dopant to move into underlying layer. Other material may be removed or remove itself (evaporate), or stay behind as separate layer and be part of final
10 structure doped or undoped.

The spatial variations of **FIGS. 12a-12c**, may be applied to the method described in connection with **FIGS. 11a-11c** so that patterns of dopant may be introduced into underlying material before top polymer film is deposited.

FIGS. 14a-14c illustrate the steps in the removal of dopant from polymer
15 film into an underlying layer. In **FIG. 14a**, substrate 19 has a bottom absorber film layer 20 deposited thereon. The absorber layer has a low chemical potential for the desired dopant. In **FIG. 14b**, the doped polymer 21 is deposited onto the absorber layer 20. In **FIG. 14c**, annealing or another cycle which causes the dopant to move is applied. In lieu of the heating treating, a solvent may be
20 applied which infiltrates (from the top) both the polymer layer 21 and the bottom layer 20 to enable the dopant in the top polymer layer to migrate into the bottom layer 20.

FIGS. 15a-15c shown the patterned addition of dopant from the top with an impermeable barrier. In **FIG. 15a**, the undoped polymer 23 is deposited on
25 substrate 22. In **FIG. 15b**, a patterned layer impermeable by the dopant 24, 25, 26 is formed on the top of the polymer 23. In **FIG. 15c** dopant 27 in ambient is heat treated by annealing. Alternatively, the structure of **FIG. 15b** may be placed into a solvent containing the dopant

FIGS. 16a-16c illustrate the application of the method described in **FIG.**
30 **12** to the formation of patterned OLEDs of different colors. As shown in **FIG. 16a**, undoped polymer 30 is deposited everywhere onto ITO layer 29 on glass substrate 28. The ITO may be patterned. Local red (31), green (32) and blue (33) regions are formed by locally doping the polymer 30. These red, green and blue

regions may be formed by ink jet printing three different solutions in different regions. Heat treating may then be applied. In FIG. 16c, top contacts 34, 35, 36 are formed on the red, green, and blue regions by standard methods such as by evaporation through a shadow mask. In making OLED's applying color dopant by using localized solvent may change any dopants which were in film from original spin coating (e.g. PBD for electron transport). So, some of this dopant may need to be put in with the color dopant solution.

FIGS. 17a-17d illustrate the application of the method described in FIG. 12 to form a passive matrix color OLED display. In FIG. 17a, ITO lines 37 are formed in one direction on glass substrate 38. In FIG. 17b, a uniform polymer film 39 is applied over the ITO lines. In FIG. 17c, red, green, blue doped polymer 40 is formed on the ITO lines in the polymer film as by the steps described in FIG. 16b. FIG. 17d cathode lines 41 as top contacts perpendicular to the bottom contact lines 37. Doping need only be in the region of the intersection of the top and bottom contact lines.

FIGS. 18a-18c illustrate the removal of dopant from polymer film in a pattern to the underlying layer. In FIG. 18a, the absorber film 43 is deposited onto substrate 42. In FIG. 18b, absorber film 43 is patterned or coated with a patterned impervious layer 44. Doped polymer 45 is added onto the layer 44. FIG. 18c shows the effect of annealing or other treatment of the structure of FIG. 18b in causing the doping to move into the underlying layer 43, where it is not impeded by the impervious barrier. The movement of the dopant may be accomplished through the use of a solvent as discussed in connection with FIG. 14c.

FIGS. 19a-19b shows the removal of dopant from the top of an unpatterned film. In FIG. 19a, doped film 47 is deposited onto a substrate 46 as by spin coating with dopant in solution. FIG. 19b illustrates the treatment of the structure of FIG. 19a by annealing in certain ambients or washing with solvent to the cause the reduction of dopant in layer 47. Washing by applying the drop may not remove the dopant from the film, but cause it to move to the edge of the drop location, leaving little dopant in the center of the drop.

FIGS. 20a-20c illustrate the patterned removal of dopant from the top of the film. In FIG. 20a, doped polymer film 49 is deposited onto substrate 48. In

FIG. 20b patterned impermeable layer **50** is applied over the doped polymer layer **49**. In **FIG. 20c**, annealing the structure of **FIG. 20b** causes dopant to evaporate in areas without barrier **50**. This evaporation may also be accomplished by washing with solvent to remove dopant in the areas without barrier **50**, or
5 treating with a solvent vapor.

FIGS. 21a-21d show the formation of an active matrix OLED display. In **FIG. 21a**, glass substrate **51** has patterned insulator **52** and electrodes **53** formed thereon. The electrodes are connect to transistors (not shown) in the pixels. In **FIG. 21b**, undoped organic layer **54** is deposited everywhere on the structure of
10 **FIG. 21a**. In **FIG. 21c**, locally applied red (**55**), green (**56**) and blue (**57**) dopant is applied as by ink jet printing. As shown in **FIG. 21d**, top electrode **58** is applied without a pattern. Top electrode **58** may be, for example Al:Li or Mg:Ag cathode.

The methods described in this invention may be applied to any organic
15 film, not just polymer based. Solvent methods may cause problems with small organic molecule based films, however, dopants could be deposited by diffusion by thermal treatment by other localized methods such as evaporation through a mask, etc.

It should be further understood that "undoped" means not doped with the
20 dopant being added or removed. Other dopants may be present.

Having thus described the invention in detail, it is to be understood that the foregoing description is not intended to limit the spirit and scope thereof. What is desired to be protected by Letters Patent is set forth in the appended claims.

CLAIMSWhat is claimed is:

1. A method for manufacturing an organic film for organic light emitting diodes, the organic film having areas with modified properties, comprising the steps of:
5 providing a substrate;
 coating an organic material thereon to form an organic film; and
 applying a dopant to areas of the film to modify the properties of the film
10 in desired areas.
2. The method of claim 1 wherein the dopant is applied by application of liquid droplets.
3. The method of claim 2 wherein the liquid droplets are applied by ink-jet printing.
- 15 4. The method of claim 2 where the substrate is heated to reduce the size of the modified area.
5. The method of claim 1 wherein the dopant is applied by screen printing.
6. The method of claim 1 wherein the dopant modifies the light emitting properties of the organic film.
- 20 7. The method of claim 6 wherein the dopant comprises red, green or blue dyes.
8. The method of claim 7 wherein the dopant includes coumarin and nile red.
9. A method of manufacturing a locally modified organic film comprising the steps of:
25 providing a substrate;
 applying an organic coating having a dopant; and
 removing the dopant from areas of the coating.
10. The method of claim 9 wherein dopant is removed from the coating by a solvent applied to a surface of the coating.
- 30 11. The method of claim 9 wherein the dopant is removed from the coating by annealing which caused the dopant to migrate from the coating.
12. The method of claim 10 wherein a mask is patterned on the coating prior to applying the solvent to remove the dopant in a pattern.

13. The method of claim 11 wherein a mask is patterned on the coating prior to annealing to remove the dopant in a pattern.
14. The method of claim 10 wherein the solvent is applied in a pattern onto the coating to remove the dopant in a pattern.
- 5 15. A method of manufacturing a locally modified organic film comprising:
providing a first layer having a dopant;
providing a second layer on the first layer; and
transferring the dopant from the first layer to the second organic layer.
- 10 16. The method of claim 15 wherein the dopant is transferred in selected areas from the first layer to the second organic layer.
17. The method of claim 16 wherein masking means is provided on the first layer prior to providing the second organic layer, and the dopant is transferred from the first layer to the organic second layer in areas not masked.
18. The method of claim 16 wherein the first layer with the dopant is
15 patterned on a substrate, and the dopant is transferred to second in the pattern of the first layer.
19. A method of manufacturing a locally modified organic film comprising of:
providing a first layer of material;
applying a dopant in a pattern to the first layer;
20 providing a second layer comprising an organic material; and
transferring the dopant from the first layer to the second layer in the pattern.
20. The method of claim 19 wherein the dopant is applied by application of liquid droplets.
- 25 21. The method of claim 20 wherein the liquid droplets are applied by ink-jet printing.
22. The method of claim 20 where the substrate is heated to reduce the size of the modified area.
23. The method of claim 19 wherein the dopant is applied by screen printing.
- 30 24. The method of claim 19 wherein the dopant modifies the light emitting properties of the organic film.
25. The method of claim 24 wherein the dopant comprises red, green or blue dyes.

26. The method of claim 25 wherein the dopant includes coumarin and nile red.
27. The method of claim 19 wherein the dopant is transferred by annealing.
28. A method of locally modifying properties of an organic film for an OLED
5 comprising the steps of:
 providing a substrate;
 applying an organic coating thereon;
 depositing a dopant or material containing a dopant thereon; and
 causing the dopant to migrate into the organic coating.
- 10 29. The method of claim 28 wherein the dopant is applied to the organic coating in a pattern, and the dopant forms the pattern in the organic layer after the dopant migrates thereinto.
30. The method of claim 29 wherein the dopant is applied by liquid droplet application.
- 15 31. The method of claim 29 wherein liquid droplets are applied by ink jet printing.
32. The method of claim 29 wherein the dopant is applied by patterning dry powder onto the organic coating.
33. The method of claim 29 wherein the dopant is applied by placing a
20 patterned thin foil containing the dopant in close contact with the organic coating.
34. The method of claim 29 wherein the dopant is caused to migrate into the organic layer by the application of heat.
35. The method of claim 30 where the substrate is heated to reduce the size of the modified area.
- 25 36. A method of manufacturing a locally modified organic film comprising the steps of:
 providing an organic film;
 covering the organic layer with a patterned barrier;
 applying a dopant or material containing a dopant over the organic layer
30 and the barrier; and
 causing the dopant to migrate into the organic film in areas exposed through the barrier.

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FIG. 1A

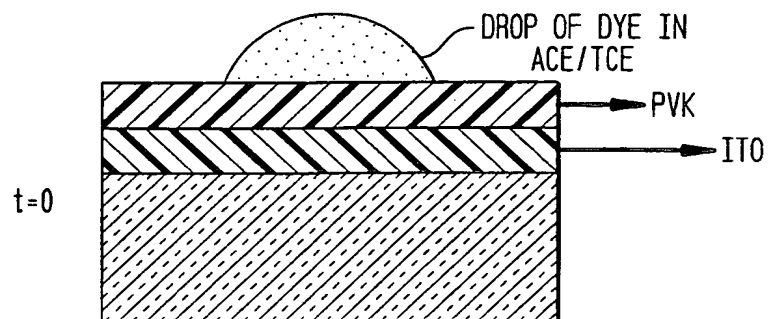


FIG. 1B

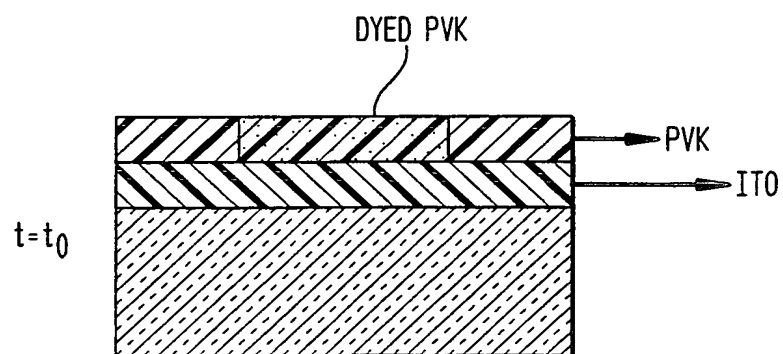


FIG. 2A

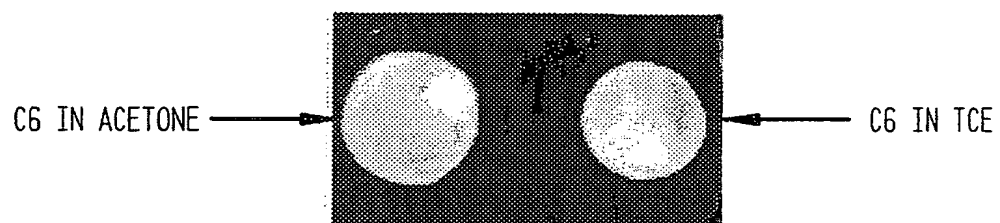
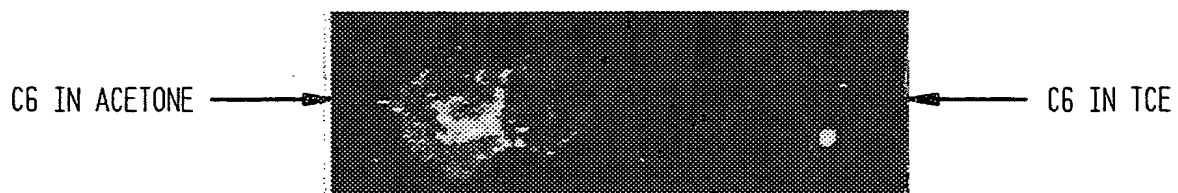
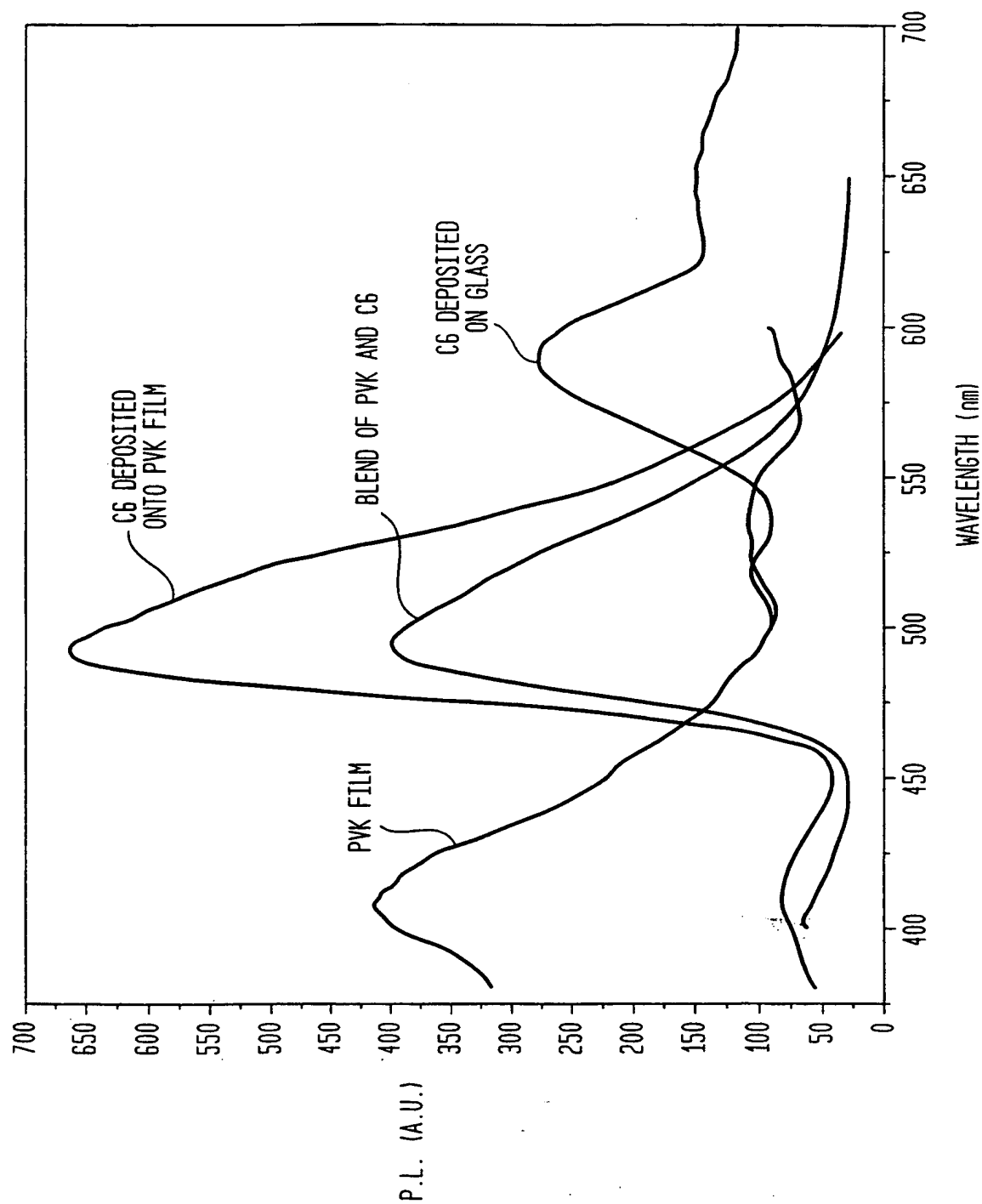


FIG. 2B



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FIG. 3



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FIG. 4A

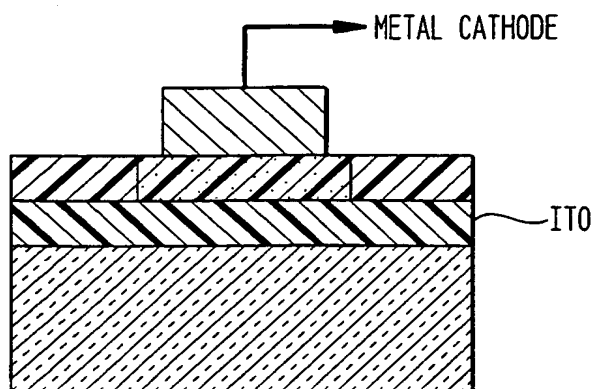
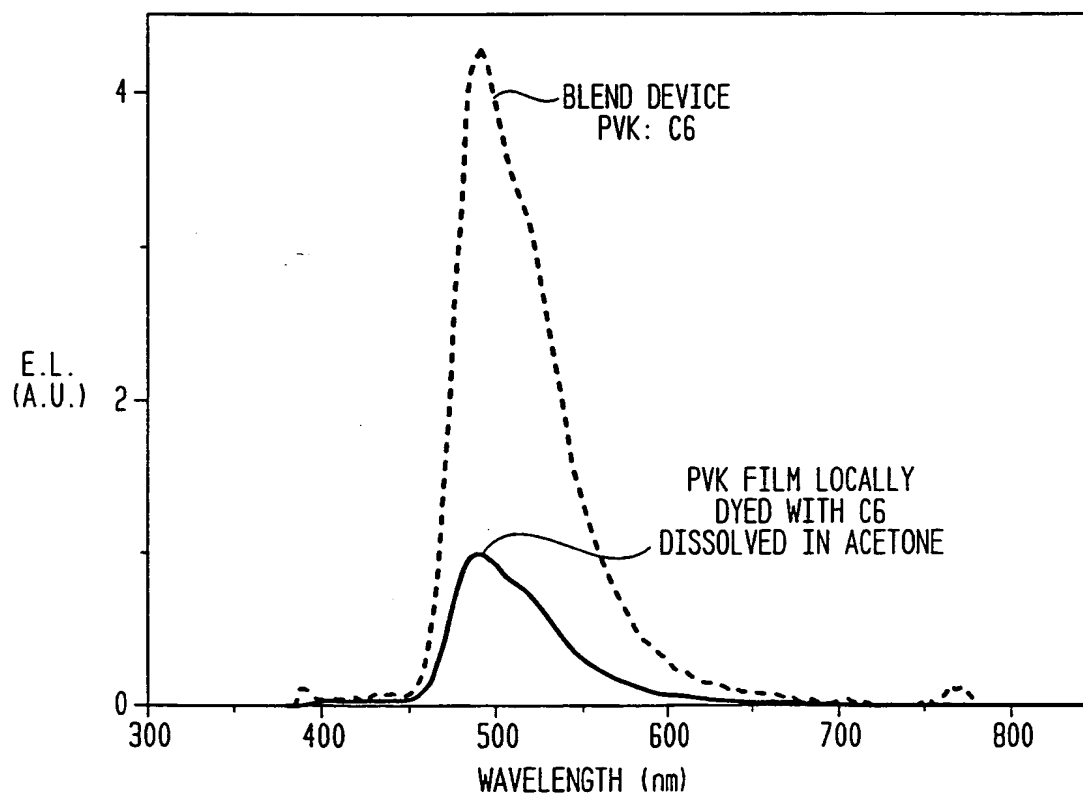


FIG. 4B



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FIG. 5A

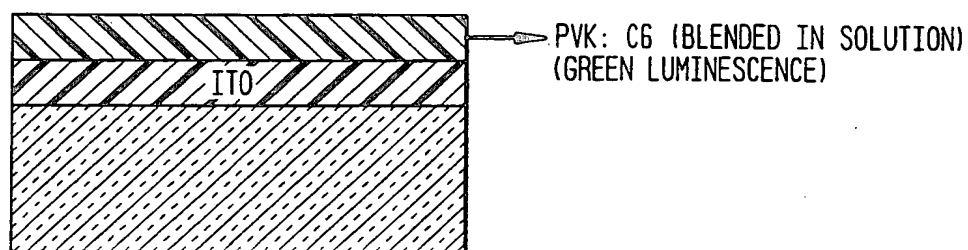


FIG. 5B

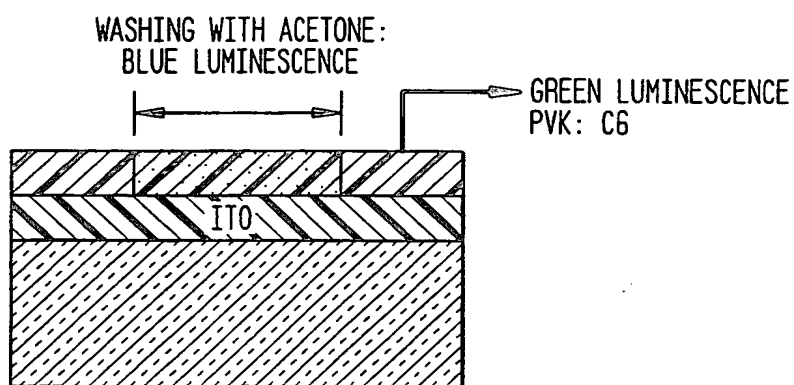


FIG. 6A

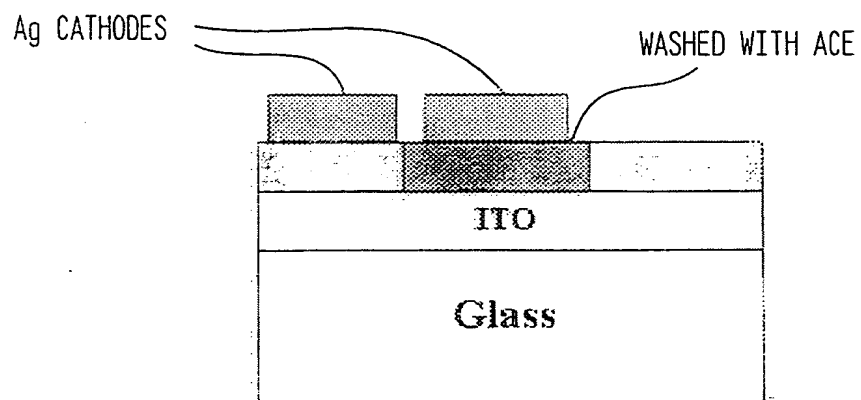


FIG. 6B

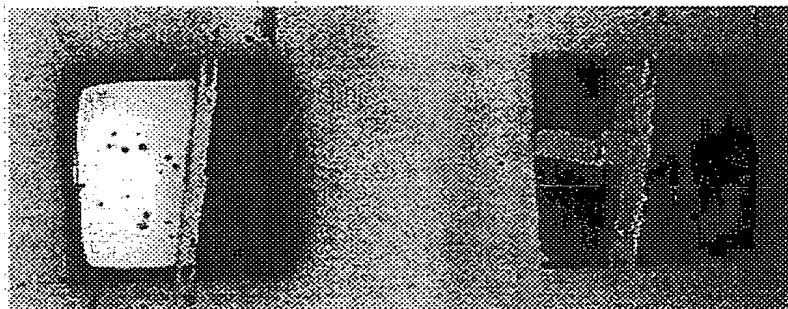


FIG. 6C

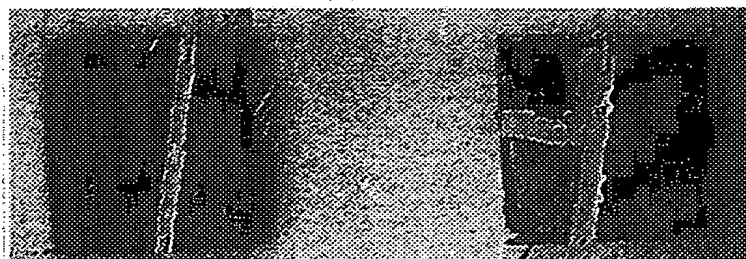
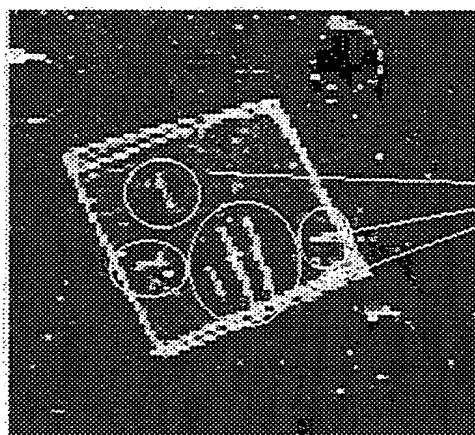


FIG. 7



LINES MADE BY
INK-JET PRINTING
OF DYE

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FIG. 8A

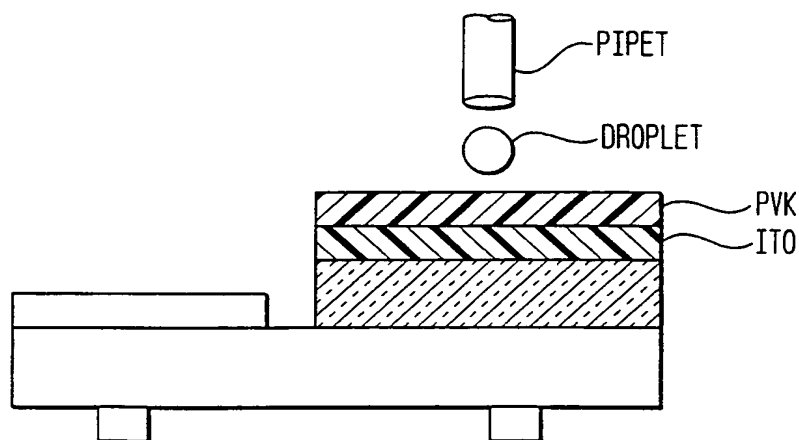


FIG. 8B

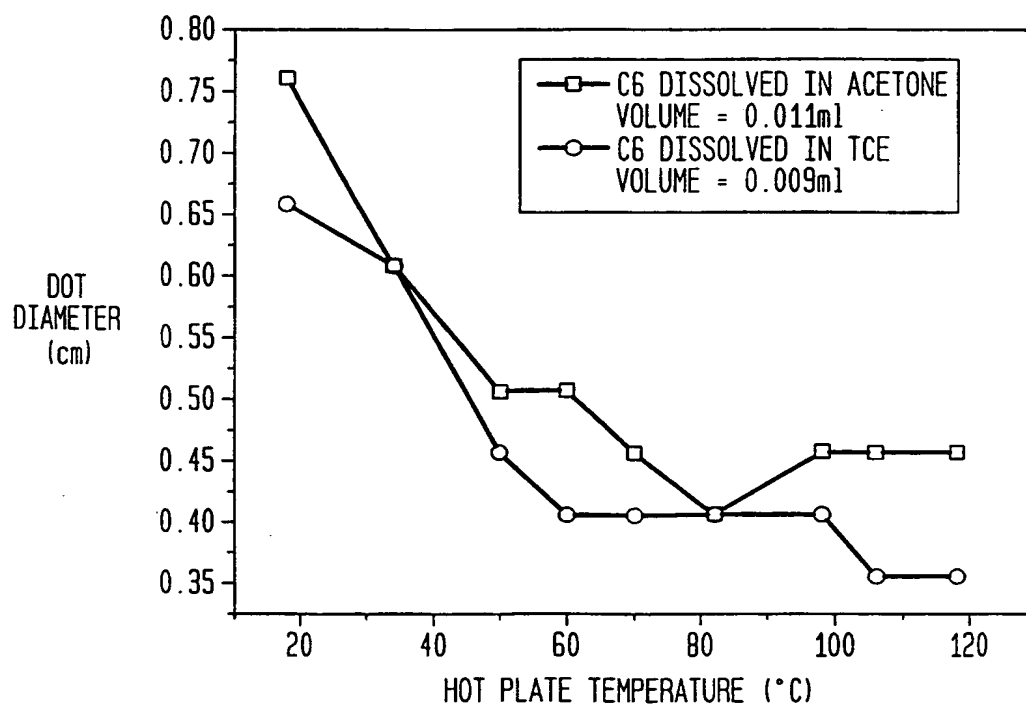
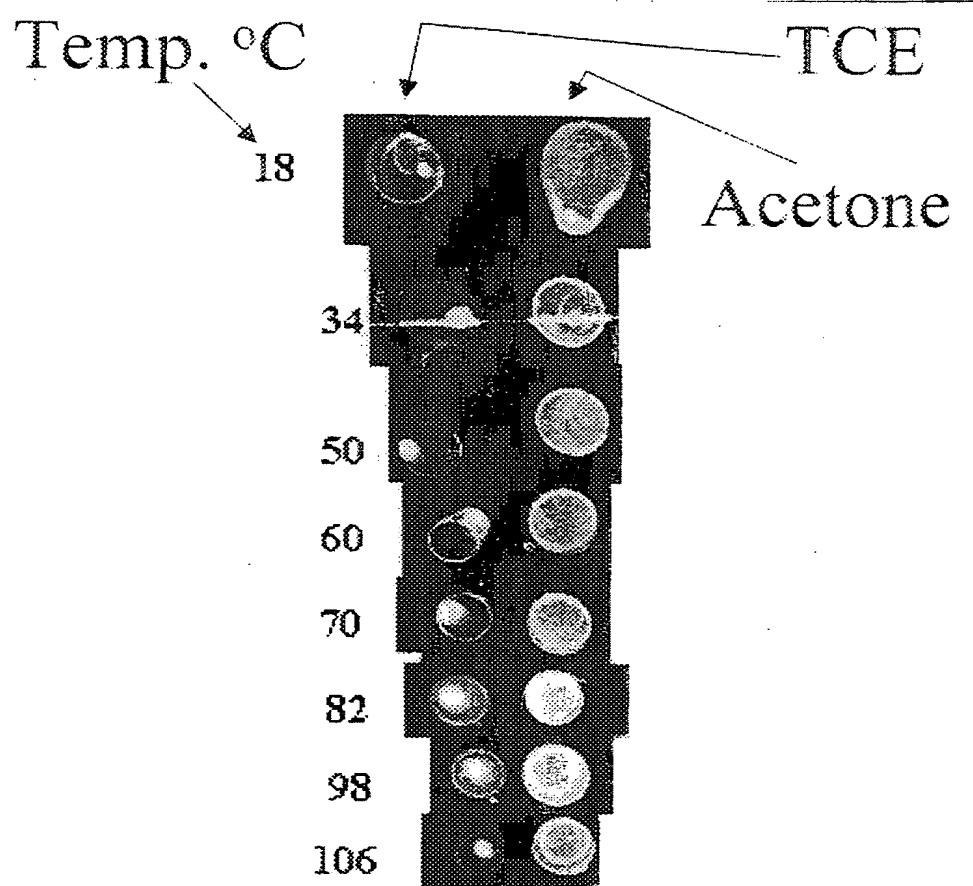


FIG. 9



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FIG. 10A



FIG. 10B

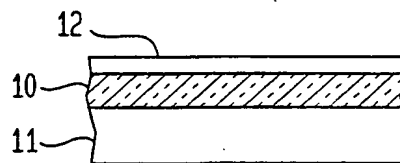


FIG. 10C

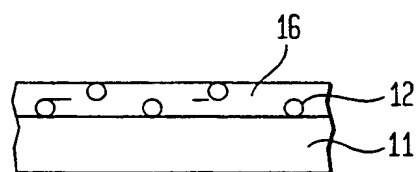


FIG. 11A

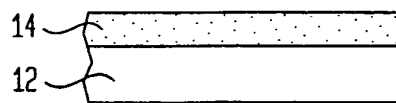


FIG. 11B

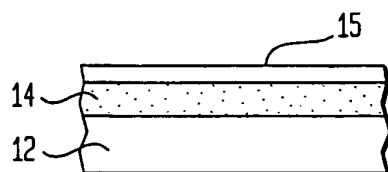


FIG. 11C

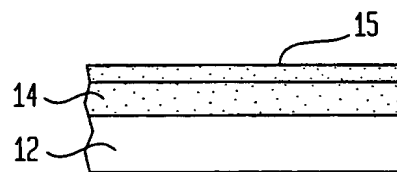


FIG. 12A

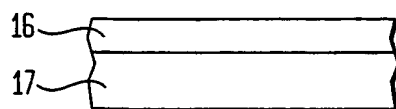


FIG. 12B

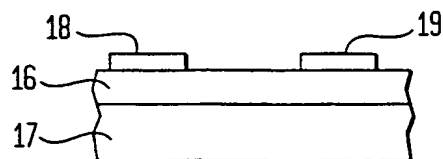
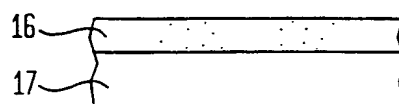


FIG. 12C



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FIG. 13A

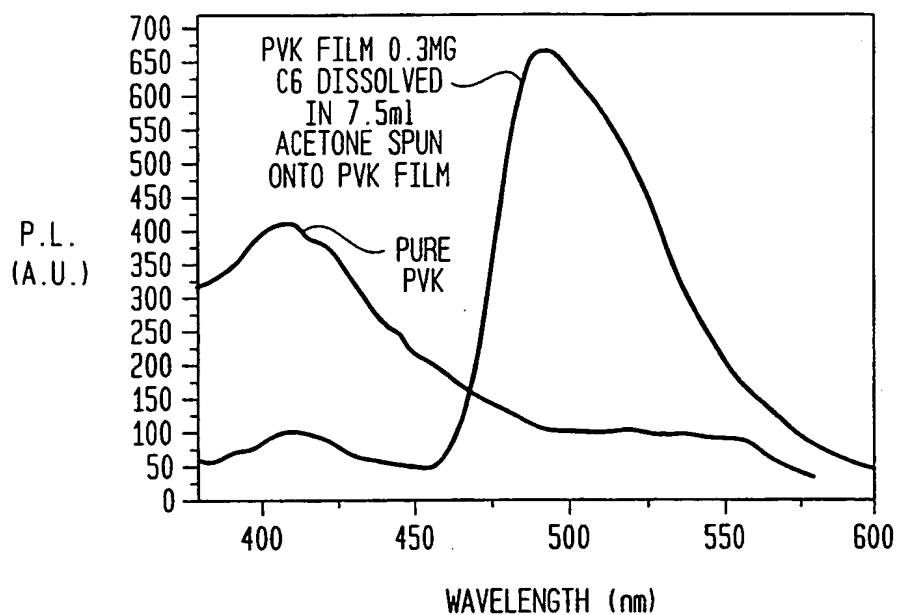
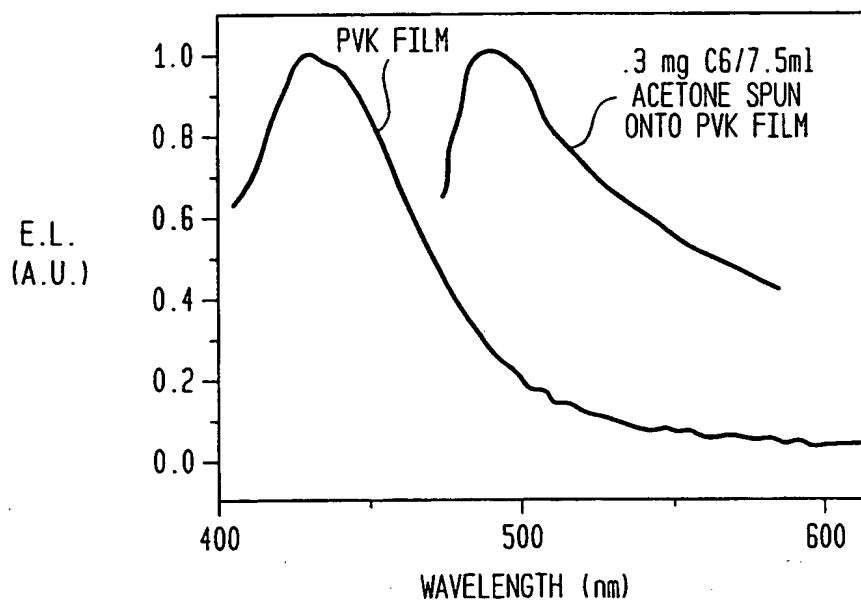


FIG. 13B



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FIG. 14A

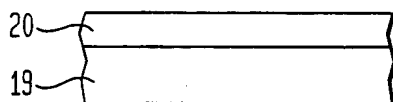


FIG. 14B

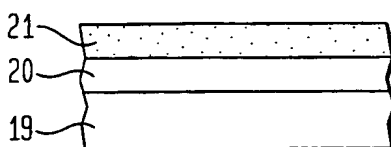


FIG. 14C

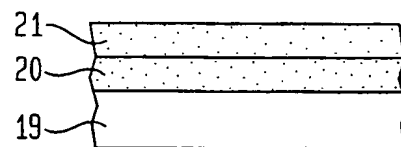


FIG. 15A

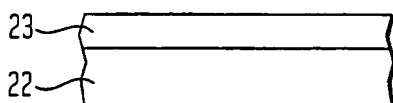


FIG. 15B

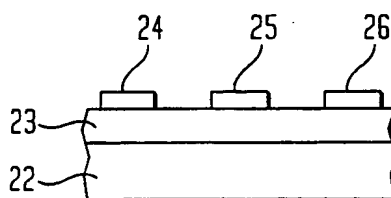


FIG. 15C

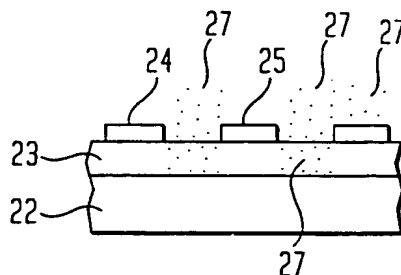


FIG. 16A

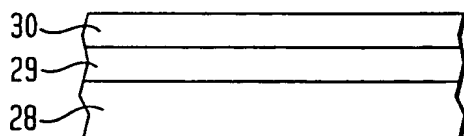


FIG. 16B

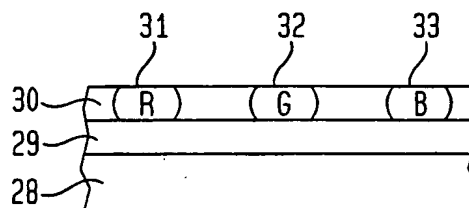


FIG. 16C

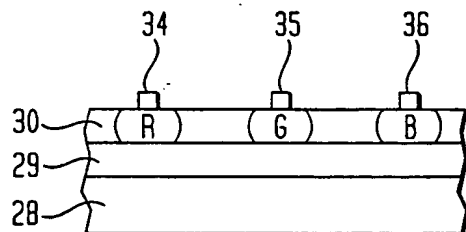


FIG. 17A

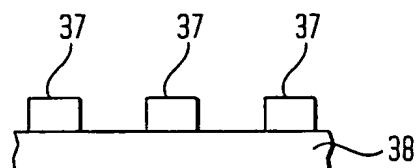


FIG. 17B

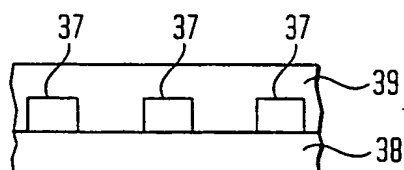


FIG. 17C

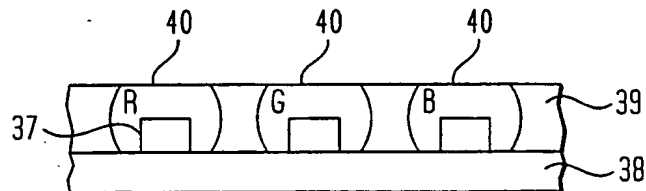


FIG. 17D

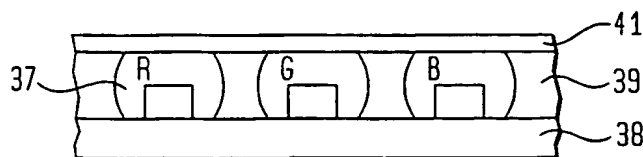


FIG. 18A

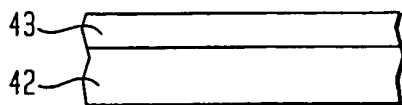


FIG. 18B

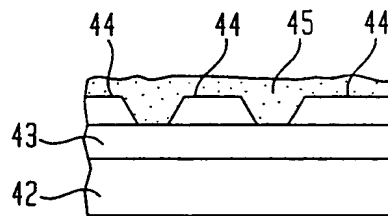


FIG. 18C

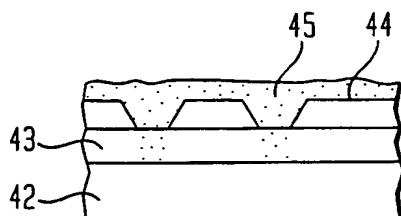


FIG. 19A

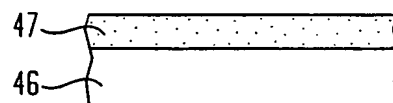


FIG. 19B

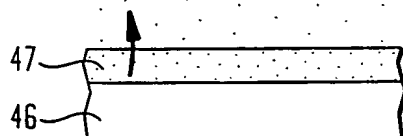


FIG. 20A

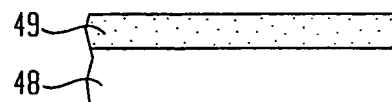


FIG. 20B

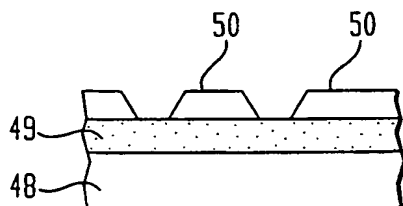


FIG. 20C

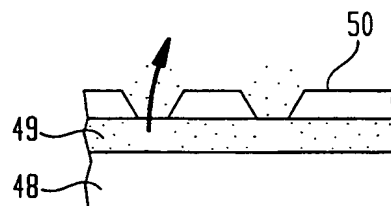


FIG. 21A

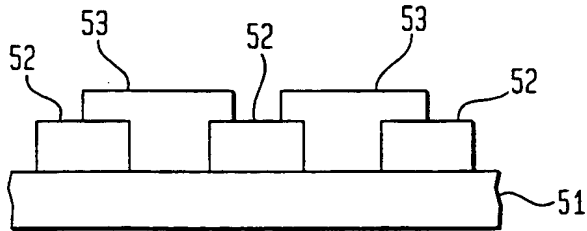


FIG. 21B

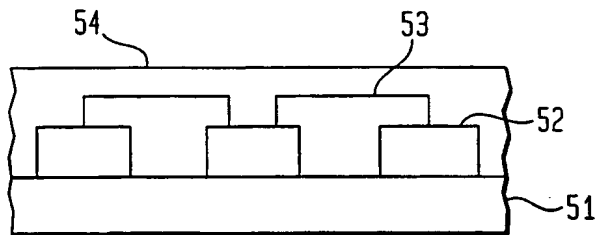


FIG. 21C

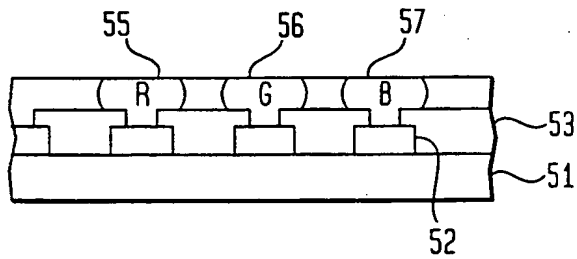
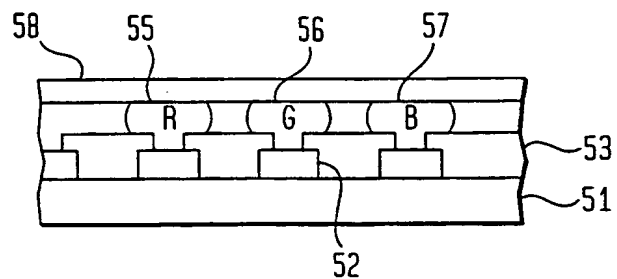


FIG. 21D

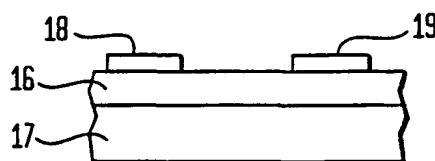




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: H01L 33/00, 21/48, 2/76, 21/223, 21/225	A3	(11) International Publication Number: WO 99/53529 (43) International Publication Date: 21 October 1999 (21.10.99)
(21) International Application Number: PCT/US99/07970 (22) International Filing Date: 12 April 1999 (12.04.99) (30) Priority Data: 60/081,492 13 April 1998 (13.04.98) US (71) Applicant (for all designated States except US): TRUSTEES OF PRINCETON UNIVERSITY [US/US]; P.O. Box 36, Princeton, NJ 08544-0036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): STURM, James, C. [US/US]; 3R Magie Apartment, Faculty Road, Princeton, NJ 08540 (US). HEBNER, Thomas, R. [US/US]; 214G Halsey Street, Princeton, NJ 08540 (US). (74) Agent: FRISCIA, Michael, R.; Friscia & Nussbaum, One University Plaza, Hackensack, NJ 07601 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> (88) Date of publication of the international search report: 20 July 2000 (20.07.00)

(54) Title: MODIFICATION OF POLYMER OPTOELECTRONIC PROPERTIES AFTER FILM FORMATION IMPURITY ADDITION OR REMOVAL

**(57) Abstract**

The methods of this invention involve modification of an organic film after it has been deposited by either adding new dopants into it from top or bottom surface, or by causing dopants to leave the film from its top or bottom surface. In the examples of these methods, the emitting color of light emitting diodes are modified based on doped polymers by locally introducing dopants causing different color emission into the film by local application of a solution containing desired dopant to the film surface (by ink-jet printing, screen printing, local droplet application, etc.). This covers the difficulties of encountered with direct patterning of three separately formed organic layers (each which uniformly coats an entire surface when formed) into regions for separate R, G, and B devices due to sensitivities of the organic materials to chemicals typically used with conventional patterning technologies. Alternatively, dopants may be introduced in an organic film (16) by diffusion from one layer (18, 19) into the film (16). Alternatively, dopants may be selectively removed from a film with solvents, etc.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/07970

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :HOIL 33/00, HOIL 21/48, HOLI 2/76; HOIL 21/223, HOLI 21/225

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 438/ 22,23, 35,45, 99, 542,548, 562, 956
257/79, 89,103Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
INSPEC, CA, WEST/BR5**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,681,756 A (NORMAN et al) 28 OCTOBER 1997 (28.10.97)(see abstract, fig.6	1-36
X	US 5,116,781 A(AGOSTINELLI et al) 26 MAY 1992(26.05.92)see abstract, col. 3, lines 38-65, col. 4, lines 44-68, col 5, lines 5-17.	9,10 1-8, 15-36
A	US 4,104,091 A (EVANS et al) 01 AUGUST 1978 (01.08.78)see abstract	1-36
X A	US 4,251,285 A(YOIDAS ET AL) 17 FEBRUARY 1981(17.02.81)See abstract detailed description	9 1-8, 10-36
X A	US 3,615,943 A (GENSER) 26 OCTOBER 1971 (26.10.71)see abstract	9 1-8,10-36



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International application No.
PCT/US99/07970

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US 5,972,052 A(KOBAYASHI et al) 26 OCTOBER 1999(26.10.99)see abstract, fig. 4.	1-36
A, P	US5,866,922 A(HUANG et al) 02 FEBRUARY 1999 (02.02.99)see abstract, fig.8	1-36
A, P	US 5,953,587 A(FORREST et al) (14 SEPTEMBER 1999 (14.09.99)see abstract, fig. 2n	1-36
A	US 5,693,962 A(Shi et al) 02 DECEMBER 1997 (02.12.97)see abstract, summary of the invention	1-36
A	US 5,583,349 A(NORMAN et al) 10 DECEMBER 1996 (10.12.96)see abstract	1--36

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/07970

A. CLASSIFICATION OF SUBJECT MATTER: US CL :

438/ 22,23, 35,45, 99, 542,548, 562, 956
257/79, 89,103